

1/PRTS

10/539715

Method for a high temperature short-time distillation of residual oil

JC17 Rec'd PCT/PTO 17 JUN 2005

Description

The invention relates to a method for high temperature short-time distillation of a residual oil originating from the processing of crude petroleum, natural bitumen or oil sand, wherein in a mixing apparatus the residual oil is mixed with granular hot coke as heat transfer medium, is converted into oil vapour, gas and coke, and gases and vapours are evacuated from the mixing apparatus while being substantially separated from the granular coke, gases and vapours are cooled down and a product oil in form of condensate as well as gas is produced and wherein the coke, which has been evacuated from the mixing apparatus, is heated again and returned into the mixing apparatus as a heat transfer medium.

Methods of this type are described in DE-C-19724074 as well as in DE-A-19959587. These methods are characterized in that the produced product oil contains pollutants, such as heavy metals (nickel, vanadium), Conradson carbon residue (CCR) as well as asphaltenes in comparison to the used residual oil only in a highly reduced concentration. This is highly advantageous for a subsequent catalytic conversion of the product oil fraction, the boiling point of which is higher than about 360°C, to benzine and gas oil in a Fluidized Catalytic Cracker (FCC). However, if the catalytic conversion of these heavy product oil fractions shall take place in a hydrocracker, the contents of pollutants of the catalyst have to be further reduced because of the higher requirements thereof.

According to experience, the remaining pollutants are concentrated in the highest boiling fraction of the product oil. Thus, a reduction of the pollutants can be principally achieved by a subsequent vacuum distillation of the product oil, that boils above 360°C, in which a pollutant bearing vacuum residue (VR) and an almost pollutant free vacuum gas oil (VGO) are obtained. A disadvantage of this method is that a vacuum distillation requires a high technical effort and can only be carried out up to certain overlapping boiling temperatures of VGO and VR in the range comprised between about 500 and 560°C. This leads to a big amount of pollutant bearing VR, which can be converted in the FCC installation but not in a hydrocracker.

On the base of this state of the art, it is the object of the invention to improve the method for high temperature short-time distillation of residual oils, such that a residual fraction, which is as small as possible and in which the undesirable catalyst pollutants are mainly concentrated, can be obtained from the product oil in a technically simple way.

According to the invention this aim is achieved in that a highly pollutant bearing residual fraction of the vapour product oil from the mixing apparatus is mixed with water vapour or gas in order to reduce the partial pressure and is then condensed at temperatures beneath  $450^{\circ}\text{C}$  in a column and is extracted while being separated from the other product oil. Afterwards, the non condensed product oil vapours from the column can be introduced into a fractionating column, in which the remaining product oil, that has a low content of pollutants, is decomposed into a VGO and a benzine/gas oil fraction (e.g. gasoline/gas oil fraction).

The invention makes use of the fact that all of the product oil is in a vapour state at the exit of the mixing apparatus and can be decomposed into the desired fractions by a fractionating condensation. For reducing the portion of highly pollutant bearing VR, the overlapping boiling range of VGO and VR has to be fixed as high as possible in a range comprised between  $450^{\circ}\text{C}$  and  $650^{\circ}\text{C}$ , such that the separated VR fraction contains more than 60% of the Conradson carbon residue (CCR), which is still contained in the product oil vapours, more than 70% of the heavy metals nickel (Ni) and vanadium (V), which are still contained in the product oil vapours, as well as more than 80% of the asphaltenes, which are still contained in the product oil vapours.

Since condensed oil fractions would quickly decompose or coke at temperatures above  $450^{\circ}\text{C}$ , the partial pressure of the oil fractions to be separated is reduced by introducing water vapour or gas into the column, such that a heavy condensate having an initial boiling point above  $450^{\circ}\text{C}$  condenses there at temperatures beneath  $450^{\circ}\text{C}$ . The condensation of VGO having a low content of pollutants (initial boiling point of about  $360^{\circ}\text{C}$ ; final boiling point of  $450$  to  $650^{\circ}\text{C}$ ) and the benzine/gas oil fraction (boiling range of  $\text{C}_5$  up to about  $360^{\circ}\text{C}$ ) can then be carried out in a second condensation stage at correspondingly lower temperatures. The thus obtained VGO having a low content of pollutants can then be catalytically converted into benzine and gas oil in a hydrocracker

and the heavy condensate can either be returned into the mixing reactor or be differently used, for example as heavy fuel oil.

Possible realizations of the method are exemplarily described by means of the drawing. Herein:

Fig. 1 is a flow chart of the method.

In Fig. 1 a heat transfer medium coke having a temperature comprised between 500 and 700°C is introduced from collecting bin (2) via pipe (3) into a mixing reactor (1). Simultaneously, residual oil having a temperature comprised between 100 and 400°C is introduced via pipe (4) into the mixing reactor (1). During mixing, a conversion temperature of the mixture comprised between 450 and 600°C is reached. The heat transfer medium coke in the mixing reactor (1) usually has a grain size in the order of 0.1 to 4 mm, such that an extensive separation of the coke from the gases and oil vapours generated in the mixing apparatus takes place at the exit of the mixing apparatus.

The mixing apparatus (1) comprises at least two intermeshing screws, which rotate in the same direction. The screws are of the type of a feed screw and have coiled conveyor paddles.

The hot, substantially oil free, granular coke leaves the mixing reactor (1) at the mixing apparatus exit with a temperature comprised between 450 and 600°C and falls through a channel (7) into a post-degasifying bin (8), into the lower part of which a strip gas (9) can be introduced. Residual gases and vapours can escape upwards from the post-degasifying bin (8) through channel (7). Excess coke is extracted via pipe (2a), wherein a part of the coke can also be extracted via pipes (12a). The coke from pipe (12) runs over a pneumatic conveyor (10), which is provided with combustion air via pipe (5) and with fuel via pipe (6), into the collecting bin (2). During the upwards conveyance by means of the pneumatic conveyor (10) a part of the coke and/or the introduced fuel is simultaneously burned. The coke, which has been heated in the pneumatic conveyor (10), reaches the collecting bin (2), from which exhaust gas is evacuated via pipe (11).

The coke in the collecting bin (2) has temperatures comprised between 500 and 700°C.

The gaseous and vaporous products of the mixing reactor (1) are introduced via pipe (13) into a cyclone (14). Here, a separation of the fine coke particles takes place, which run via pipe (15) into the post-degasifying bin (8).

The gaseous and vaporous products flow from cyclone (14) through pipe (16) into a column (17), where they are quenched and thus cooled down from 450 through 600°C to 350 through 450°C.

Returned C<sub>4</sub> product gas from vessel (23) or water vapour is introduced via pipe (24a) into the head of column (17). This reduces the partial pressure of the vapour product oil to such an extent that a heavy oil fraction having an initial boiling point between 450 and 650°C, in which nearly all pollutants are concentrated, condenses there at 350 – 450°C. Decomposition or coking of the condensed oil is thus prevented. The column is preferably a quench cooler with a downstream multi-venturi washer, in which the gases and vapours originating from the mixing reactor (1) are very efficiently cooled in a parallel flow and residual breeze is washed out with its own condensate. But other apparatuses can also be used for this purpose.

For reducing the portion of heavy oil having a high content of pollutants, the overlapping boiling range of VGO and VR is set at a temperature as high as possible and comprised between 450 and 650°C. This is achieved by introducing gas or water vapour into the head of column (17) via pipe (24a) and by cooling the gases and vapours by means of cooled heavy oil condensate from pipe (27a). The heavy oil condensate having a temperature comprised between 350 and 450°C is extracted from the basin of column (17) via pipe (27), cooled down to the required temperature in a heat exchanger (25) and partially returned as cooling/washing medium to the head of column (17). The other part of the heavy oil condensate is extracted as product via pipe (27b). The heavy oil condensate from pipe (27b) can afterwards either be returned to the mixing reactor (1) or be differently used, for example as heavy heating oil.

The non condensed gas/oil vapour mixture is extracted from the lower part of column (17) via pipe (18). According to another realization of the invention, it can be introduced

into a fractionating column (19). There, the remaining product oil is separated into VGO having a low content of pollutants and a pollutant free benzine/gas oil fraction. The VGO having a final boiling point of 450 – 650°C is extracted via pipe (21) from the bottom of the fractionating column (19). The thus obtained VGO can afterwards be catalytically converted into benzine and gas oil in a non represented hydrocracker. The remaining gas/oil vapour mixture from the head of the fractionating column (19) is cooled in condenser (22) via pipe (20) and separated in vessel (23) into a benzine/gas oil fraction having a boiling range of e.g. C<sub>5</sub> – 360°C and a C<sub>4</sub> gas. The benzine/gas oil fraction is extracted via pipe (26) and partially returned to the head of the fractionating column (19) via pipe (26b). The remaining benzine/gas oil mixture is evacuated as product via pipe (26a).

Non condensed C<sub>4</sub> gas is evacuated upwards from vessel (23) via pipe (24) and partly returned into column (17) via pipe (24a) and partly extracted as product via pipe (24b).

### Example

100 t/h residual oil having a temperature of 300°C are introduced into the mixing reactor (1) via pipe (4). 75 t/h gas/oil vapour mixture having a temperature of 550°C are introduced from mixing reactor (1) via pipe (13) into a cyclone (14) for dedusting. The remaining 25 t/h coke, together with heat transfer medium coke, are introduced via pipe (7) into the post-degasifying bin (8).

The gas/oil vapour mixture is routed from cyclone (14) via pipe (16) into a column (17), where it is diluted with gas and cooled down from 550°C to 425°C. For this, column (17) is provided with 43 t/h C<sub>4</sub> gas from pipe (24a) and 55 t/h cooled heavy oil condensate having a temperature of 380°C from pipe (27a).

65 t/h heavy oil condensate having an initial boiling point of 600°C are extracted via pipe (27) from the bottom of column (17) and cooled down from 425°C to 380°C in a heat exchanger (25). Afterwards, 55 t/h cooled heavy oil condensate are returned to the head of column (17) via pipe (27a) and 10 t/h are extracted as product via pipe (27b).

108 t/h non condensed gas/oil vapour mixture are introduced from the lower part of column (17) via pipe (18) into a fractionating column (19). 40 t/h VGO having a low content of pollutants and a temperature of 350°C are extracted from the bottom of the fractionating column (19) via pipe (21). The remaining 68 t/h gas/oil vapour mixture are extracted from the head of the fractionating column (19) via pipe (20), cooled down to 43°C in a condenser (22), introduced into vessel (23) and separated there into a liquid benzene/gas oil fraction having a boiling range of C<sub>5</sub> – 360°C and a C<sub>4</sub> gas. 53 t/h C<sub>4</sub> gas are extracted via pipe (24) and 43 t/h thereof are returned into the head of column (17) via pipe (24a). The remaining 10 t/h C<sub>4</sub> gas are extracted as product via pipe (24b). Furthermore, 15 t/h benzene/gas oil mixture are extracted as product via pipe (26a).

In a single-stage condensation according to the state of the art, one would obtain 50 t/h residue having an initial boiling point of 360°C instead of 10 t/h heavy oil condensate having an initial boiling point of 600°C. Even with an extensive vacuum distillation, one could only obtain 20 t/h VGO having a low content of pollutants and a boiling range comprised between 360 and 510°C from the residue according to the state of the art. However, according to this invention, 40 t/h VGO having a low content of pollutants and a boiling range comprised between 360 and 600°C, i.e. the double quantity, can be obtained in a technically simpler manner.